

Predicting and Understanding Novel Electrode Materials From First-Principles

Kristin Persson

Principal Investigator, Project ID ES091
Lawrence Berkeley National Laboratory, Berkeley, California
94720

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Timeline

- Start Date Oct 2016
- End Date: October 2020

Budget

- Total budget (4 years): \$1,300K
- FY16 funding \$350K

Barriers Addressed

- Inadequate Li-ion battery energy density, cycle life and rate
- High cost of electrode materials

Partners/Collaborations within the VT program

- Project lead: **Vince Battaglia** (LBNL)
- **Vince Battaglia** (LBNL), **Robert Kostecki** (LBNL), **Guoying Chen** (LBNL) and **Gerbrand Ceder** (UCB): understanding degradation mechanisms in Li-excess materials and optimizing Li ion electrolytes

Relevance

The Li-excess cathode materials exhibit more than 200 mAh/g initial capacity but also insufficient cycling performance, voltage fade, and long-time structural degradation

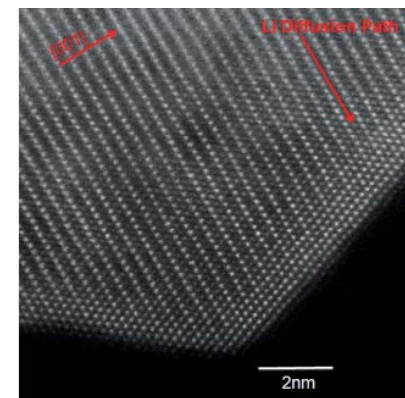
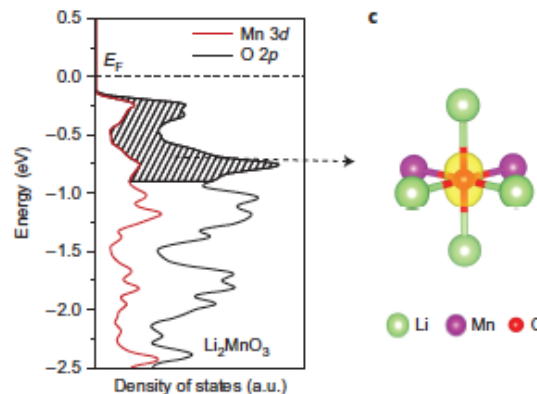


Fig. 5 High resolution S/TEM image (a) and corresponding HAADF image (b) of the bulk and surface regions of electrochemically cycled Li [Ni_{1/3}Li_{1/3}Mn_{1/3}]O₂ taken along the [110] zone axis.

Ceder et al, Nat Chem 8 692 (2016), Persson et al Adv. Energy Mater. 2014, 4, 1400498

Meng et al., EES 4, 2223 (2011)

Redox activity on the oxygen in Li-excess materials leads to increased oxygen loss from surface; extensive surface reconstructions and impeded charge transfer

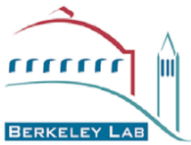
Objectives:

- Understanding the degradation mechanisms related to the release of surface oxygen of target cathodes as a function of charge
- Suggesting surface protection procedures based on first-principles investigations

Relevance:

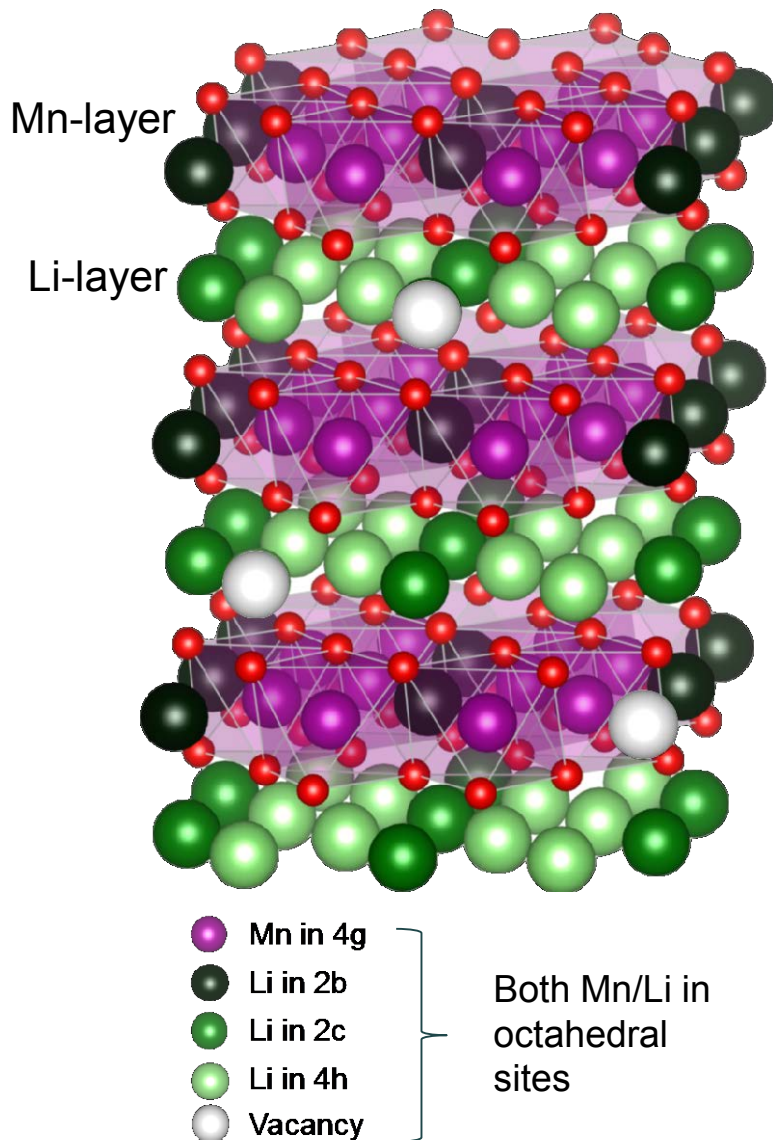
- To investigate synthesis and post-synthesis processes (doping, coatings) possible to increase the stability of the material

Milestones



Month Year	Milestone	Status
October 2016	Provide matrix of surface candidate dopants based on literature search and practical considerations	Complete
	Benchmark calculations of amorphous coating materials i.e. $\text{Al}_2\text{O}_3/\text{SiO}_2$	Complete
June 2017	Present first screening of surface dopants	Complete
September 2017	<u>Go/No-Go</u> : Stop this approach if facet stabilization can not be achieved.	Ongoing

Li_2MnO_3 crystal structure



Li and Mn-rich compositions yield high capacity but correlates with the chemical and structural degradation of Li excess materials. During previous years, the origin of the degradation was elucidated and now mitigation strategies are explored

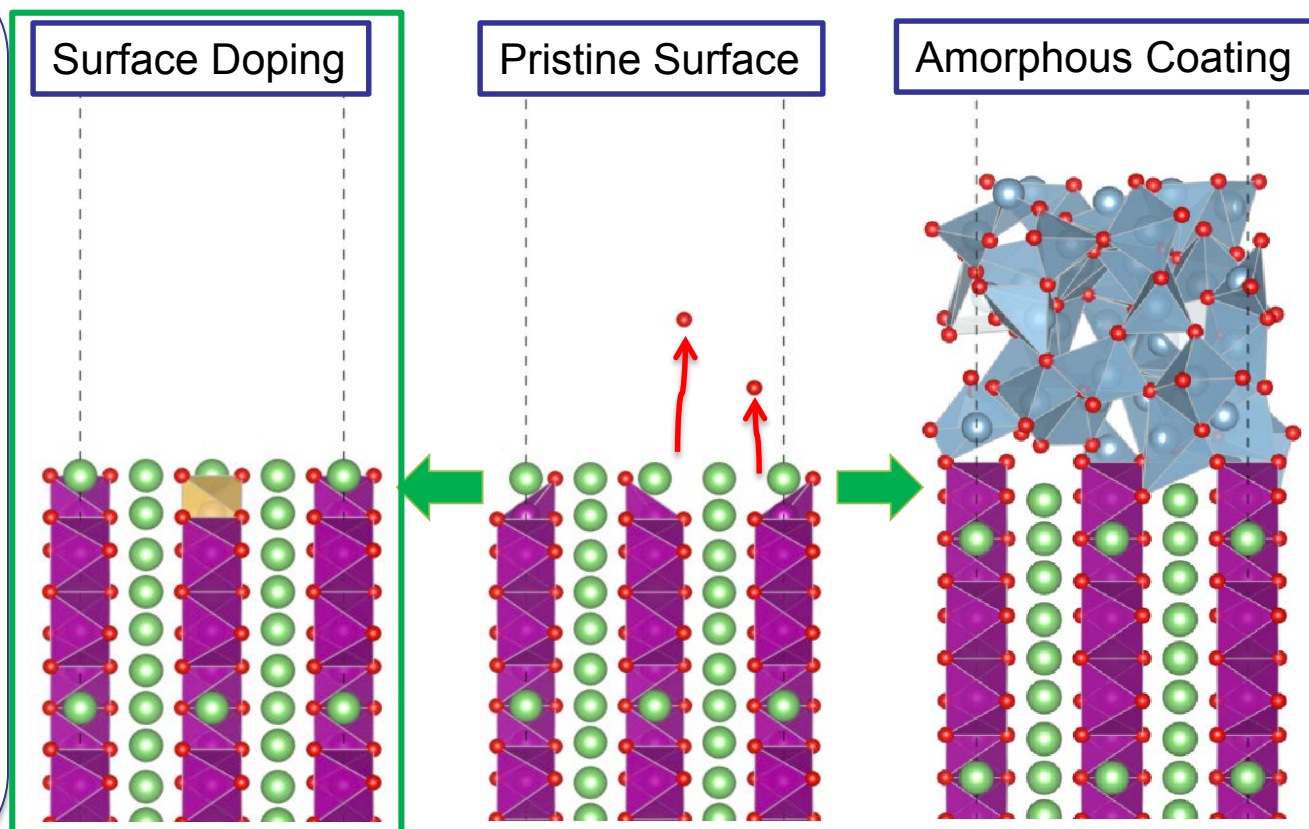
- Li_2MnO_3 is taken as a model worst-case scenario of the Li-excess, Mn-rich materials.
- Bulk calculations showed that **Li mobility is excellent in *pristine* material**. However, **bulk Mn migration and surface oxygen loss will both contribute to impeded transport and voltage/capacity degradation**.

Y. Shin, H. Ding and K. A. Persson, *Chem. Mater.*, **2016**, 28 (7), pp 2081–2088 and Y. Shin and K. A. Persson *ACS Appl. Mater. Interfaces*, **2016**, 8 (38), pp 25595–25602

Approach (2)

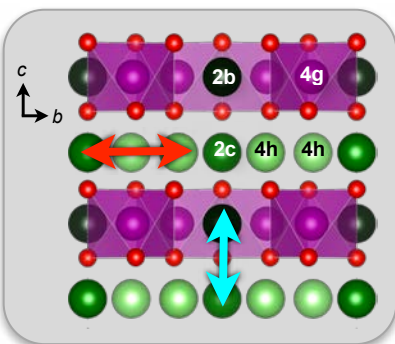
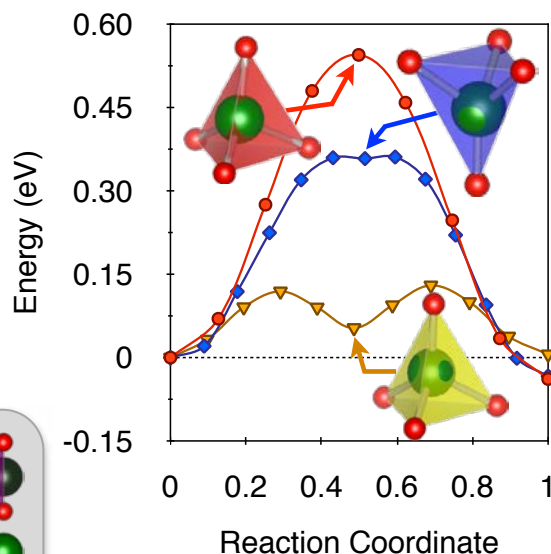
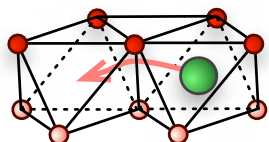
All Li_xMnO_3 surfaces were found to exhibit a thermodynamic driving force for oxygen release at Li concentrations < 1.7 . To mitigate oxygen release, Li-excess cathodes may be protected through post-synthesis processes such as **surface doping or coating**.

- Surface doping can be an effective approach to protect the surface from spontaneous oxygen evolution without impeding the Li mobility
- Surface coatings that possess an amorphous morphology lack grain boundaries can enable oxygen retention through limited oxygen mobility and enhanced stability

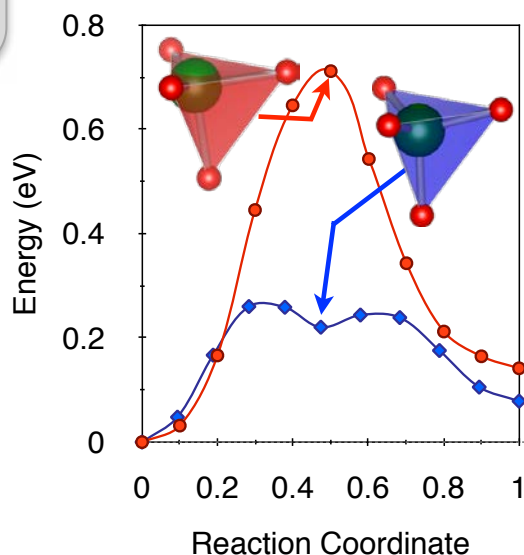
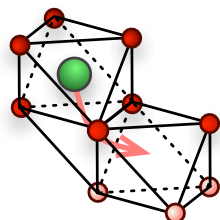


Technical Accomplishments (1)

Intra-layer
(a-b direction)



Inter-layer
(c direction)



Bulk Property

The ***pristine*** Li_xMnO_3 ($1 \leq x \leq 2$) material exhibits excellent Li mobility enabling facile Li extraction from both the transition metal layer and Li-layer.

- Intra-layer Li migration has similar behavior and activation barriers as LiCoO_2
- Extremely favorable inter-layer Li-ion migration activated by di-vacancies
- Mn migration into Li-layer degrades inter-layer mobility

Technical Accomplishments (2)

Low Miller index Wulff shape of Li_2MnO_3

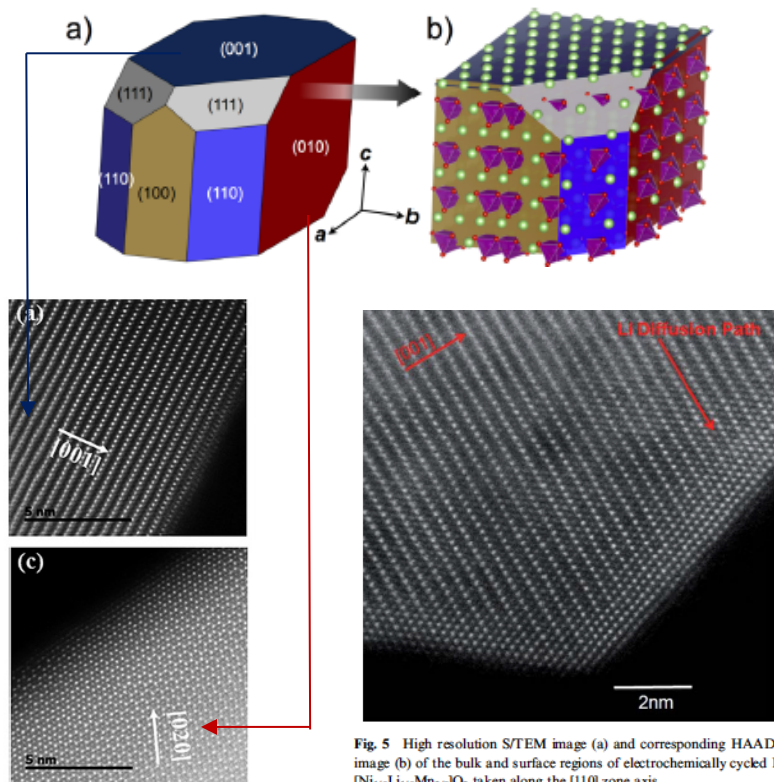
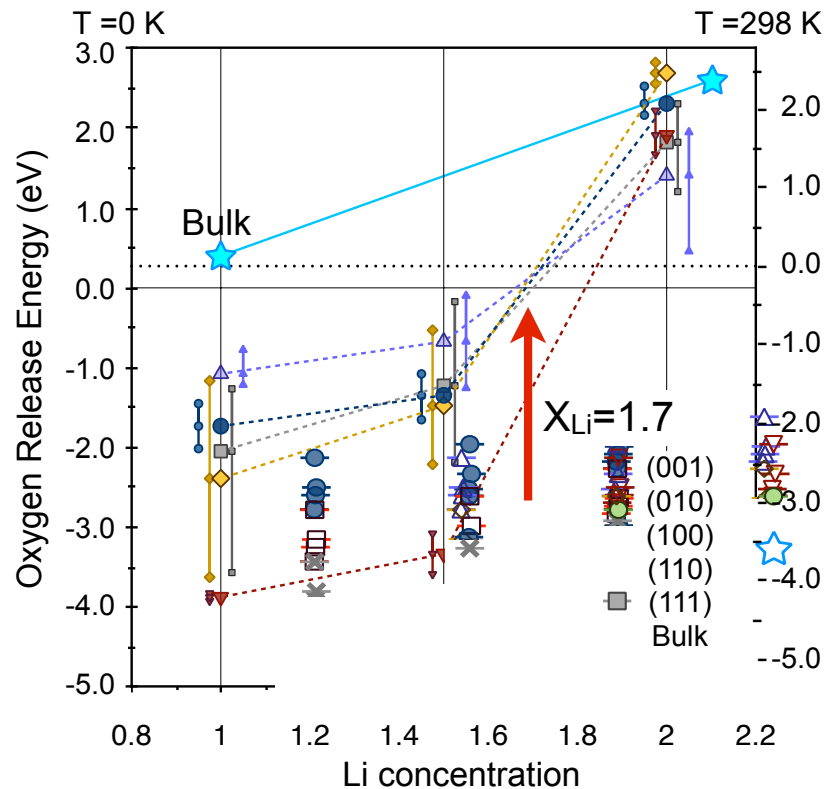


Fig. 5 High resolution S/TEM image (a) and corresponding HAADF image (b) of the bulk and surface regions of electrochemically cycled $\text{Li}[\text{Ni}_{1/3}\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ taken along the [110] zone axis.

Kim et al ChemSusChem -
2015, 8, 3255 – 3262

Meng et al., EES 4, 2223 (2011)

Oxygen release energies on each surfaces



Exp.: Oxygen evolution initiates at 19% of Li extraction (i.e., $\text{Li}_{1.63}\text{MnO}_3$)

- Calculated Wulff shape shows that dominant surfaces are (001), (110), and (010). Experiments show evidence of both (001) and (010) layered surface facets.
- **All surface facets are predicted to lose oxygen past $x = 1.7$. The (011) surface exhibits the best oxygen retention as a function of Li loss.**

Y Shin and K. A. Persson ACS Appl. Mater. Interfaces, 2016, 8 (38), pp 25595–25602
Peer Review, Washington 2017

Technical Accomplishments (3)

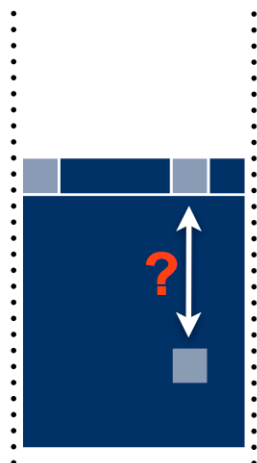
Computational surface dopant screening includes 1) dopant segregation, 2) defect formation, and 3) oxygen evolution.

Dopant Segregation

Investigate the defect position preference between bulk and each surface for given dopant

$$E_S = \left(\left| \begin{array}{c} \text{dopant} \\ \text{surface} \end{array} \right| - \left| \begin{array}{c} \text{dopant} \\ \text{bulk} \end{array} \right| + \left| \begin{array}{c} \text{surface} \\ \text{vacancy} \end{array} \right| - \left| \begin{array}{c} \text{bulk} \\ \text{vacancy} \end{array} \right| \right)$$

$$E_S = \Delta E^{bulk} - \Delta E^{surface}$$

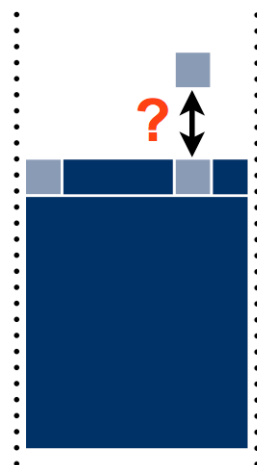


Defect Formation

Represent the surface defect formation energy above the convex hull

$$E_D^S = \left(\left| \begin{array}{c} \text{dopant} \\ \text{surface} \end{array} \right| - \left| \begin{array}{c} \text{dopant} \\ \text{bulk} \end{array} \right| + \left| \begin{array}{c} \text{surface} \\ \text{vacancy} \end{array} \right| - \left| \begin{array}{c} \text{bulk} \\ \text{vacancy} \end{array} \right| \right) - E_{PD}^{eq}$$

$$E_D^S = (\Delta E^{surface} + E^{bulk}) - E_{PD}^{eq}$$

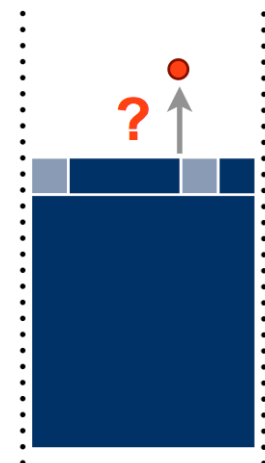


Oxygen Evolution

Calculate the oxygen evolution on each surface facet


$$\tilde{E}_O = \left(\left| \begin{array}{c} \text{oxygen} \\ \text{surface} \end{array} \right| + \left| \begin{array}{c} \text{surface} \\ \text{vacancy} \end{array} \right| - \left| \begin{array}{c} \text{bulk} \\ \text{vacancy} \end{array} \right| \right)$$

$$\tilde{E}_O = E_{O-x'}^{slab} + \Delta\mu_O - E^{slab}$$



Technical Accomplishments (1)

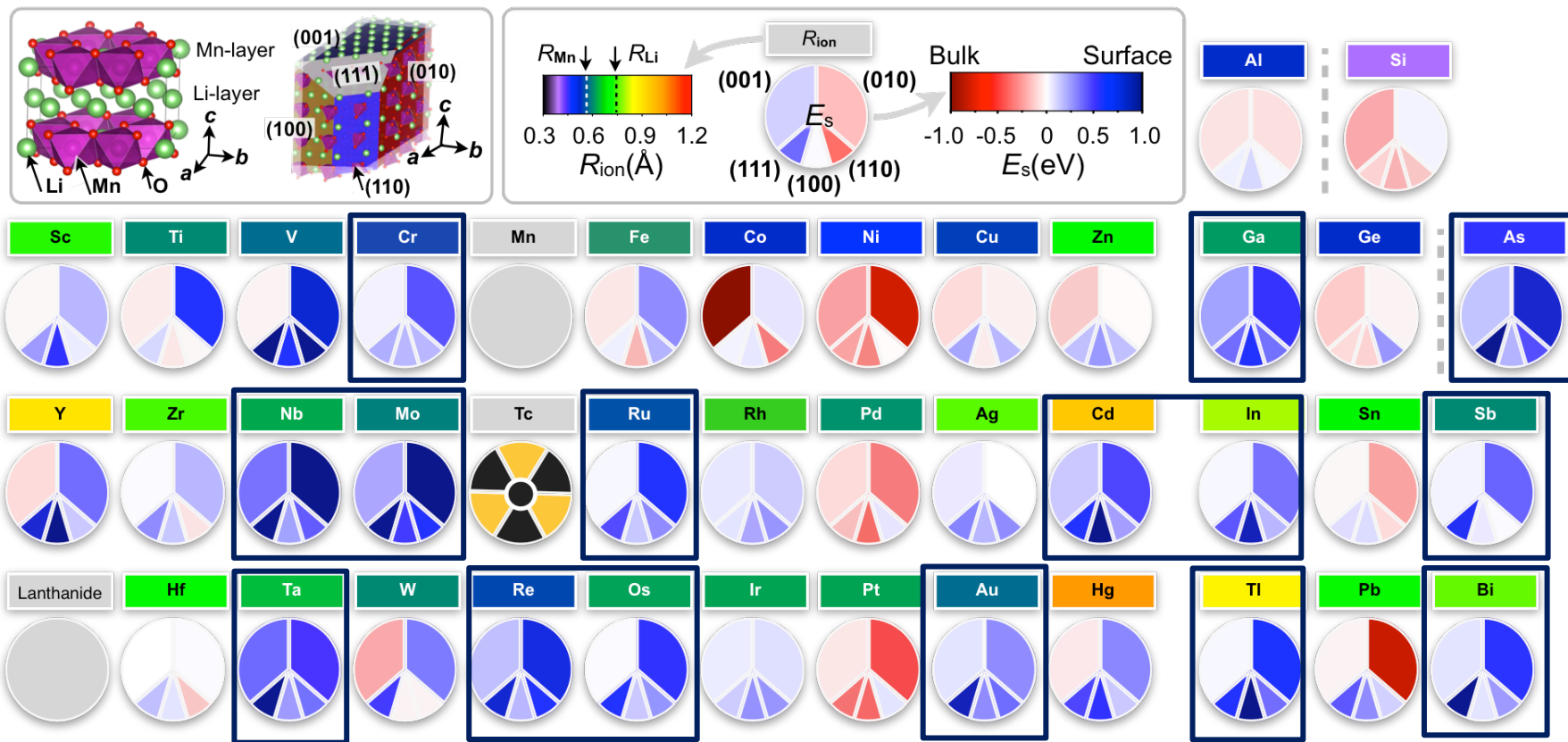
Periodic Table of the Elements

																		Atomic Number		Valence Charge			
																		Symbol		Name		Atomic Mass	
1 IA 1A H Hydrogen 1.008																		18 VIIIA 8A He Helium 4.003					
3 Li Lithium 6.941	4 Be Beryllium 9.012																	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948						
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798						
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294						
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018						
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown						

- The surface doping elements exploration includes all transition metals, post-transition metals, and metalloids.
- All possible low miller index surfaces are examined

Technical Accomplishments (3)

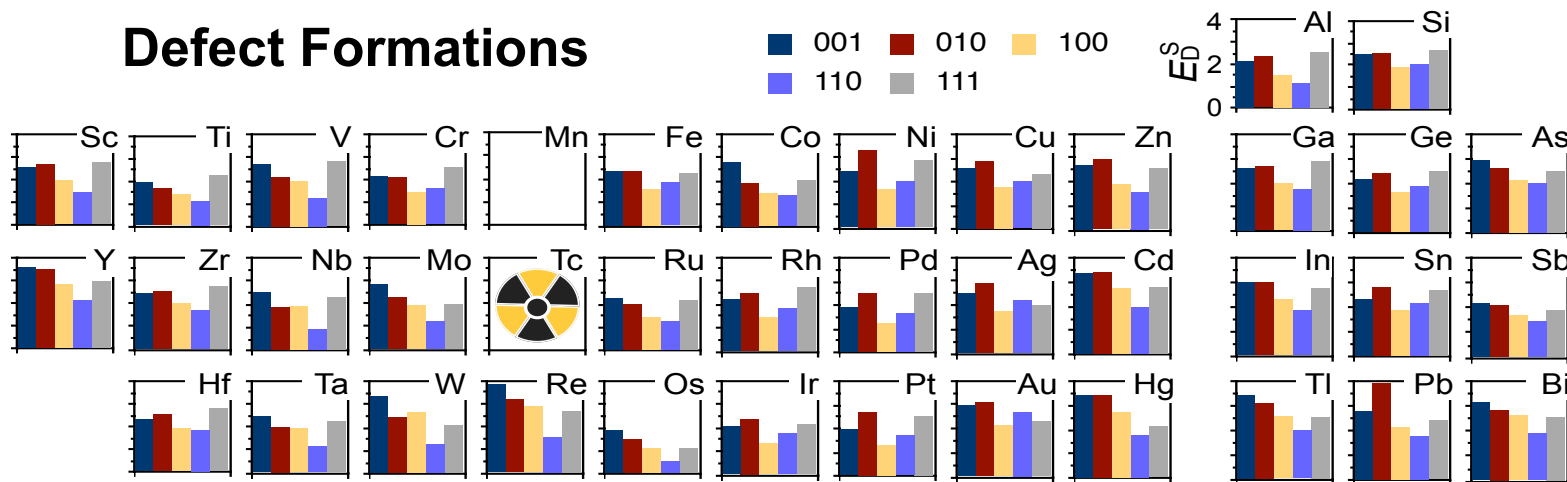
Dopant Segregations -



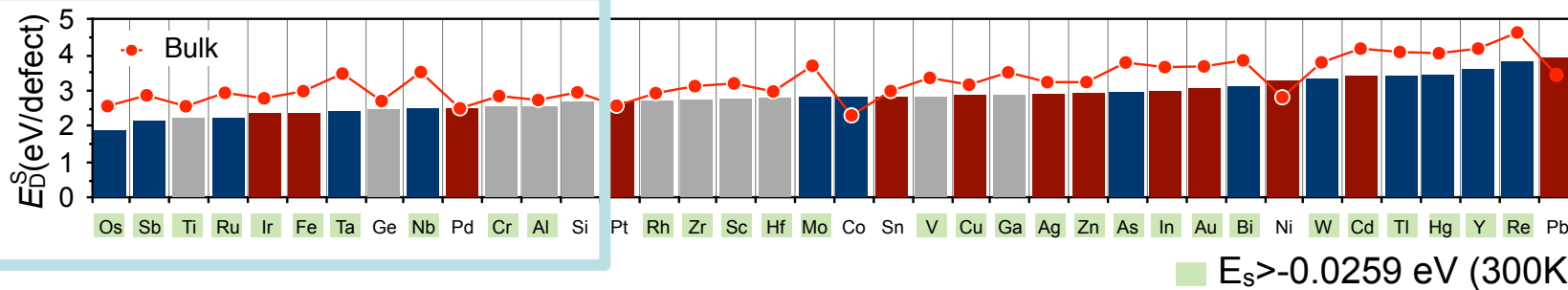
- Dopant segregation energy depends on the specific surface facet.
- Elements with strong surface segregation energy for all facets (outlined in blue) are good candidates as dopant will preferentially segregate to the surface of the material.

Technical Accomplishments (4)

Defect Formations



Average surface dopant formation energy



Surface dopant concentration will compete with creation of secondary impurity phases during synthesis. Hence, we screen on the surface defect formation energy (E_D^S).

- Defect dopant formation energy is dependent on the specific surface facet.
- Lower formation energy is favorable ; focus on framed elements

Technical Accomplishments (5)



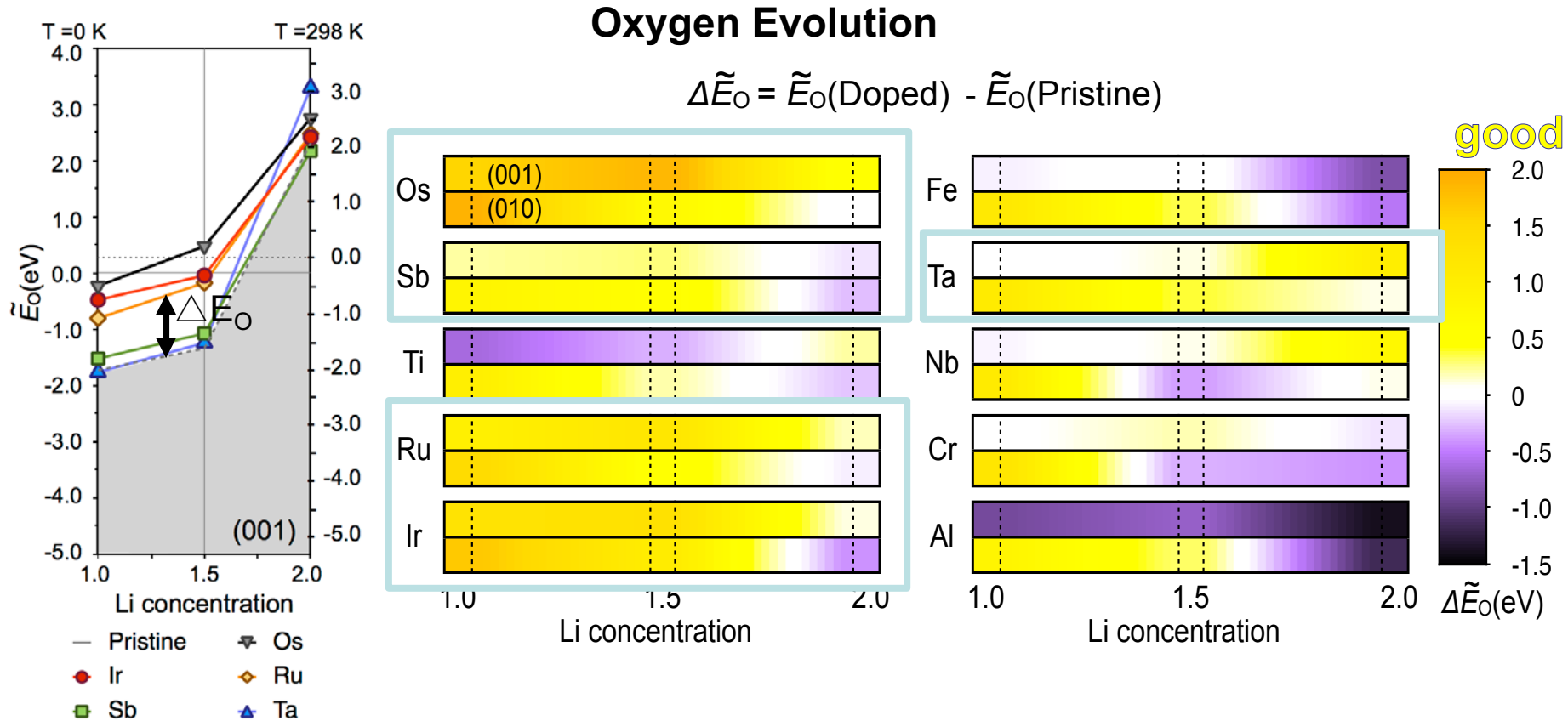
Taking the union of elements which

- i. - preferentially segregate to the surface (rather than the bulk) of a Li-excess Mn-rich layered oxide
- ii. - are *less likely* to form secondary impurity phases -



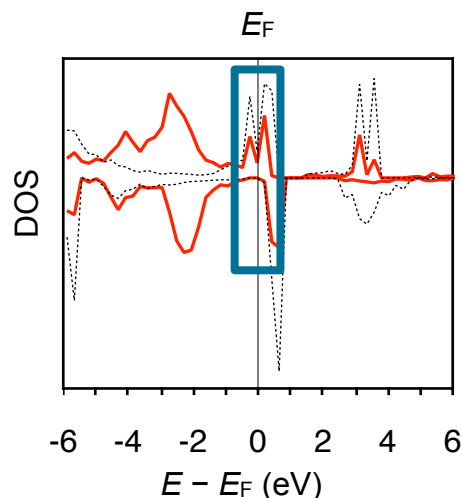
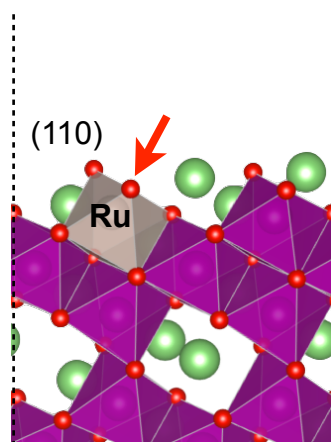
Os, Sb, Ti, Ru, Ir, Fe, Ta, Nb, Cr, Al -

Technical Accomplishments (6)

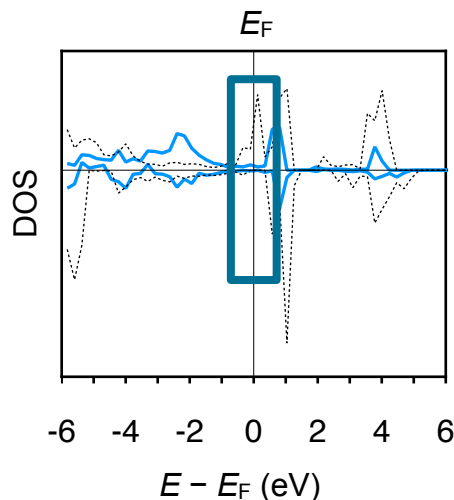
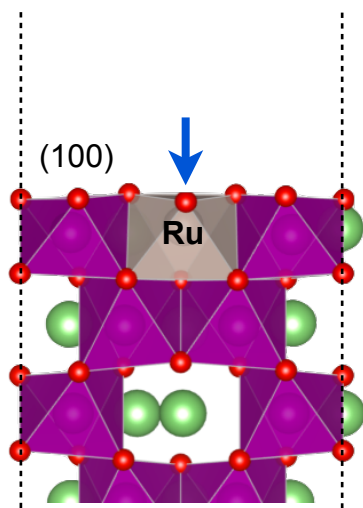


Select dopant elements that exhibit large oxygen retention energy (positive energy: yellow bar)
 *PI Guoying Chen is experimentally verifying the surface doping driven oxygen protection using Ta doping $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ surfaces.

Technical Accomplishments (7)



Overlapping, strong hybridization between the oxygen p-orbitals (dashed line) and the surface defect d-orbitals (red line) preventing spontaneous oxygen evolution.



Non-overlapping, de-hybridized oxygen p-orbitals (dashed line) and surface defect d-orbitals (blue line) explains less surface oxygen retention effect

• To enhance the performance of Li-ion systems, improvements on the cathode and the electrolyte side are needed. This project is aimed to result in an improved understanding of the atomistic mechanisms underlying the surface behavior and performance of the Li-ion cathode materials with the ultimate goal being to suggest strategies, such as coatings, surface protection and particle morphology design.

Using first principles modeling on Li-excess, Mn-rich cathode materials; we have established that:

- - The pristine material exhibits excellent Li mobility enabling facile Li extraction from both the transition metal layer and Li-layer.
- All low miller index surfaces of Li_xMnO_3 exhibit spontaneous oxygen evolution during charge (for $x < 1.7$) pointing to a likely culprit for materials degradation and increased impedance.
- Surface dopants are investigated to increase oxygen retention. The candidate dopants are screened by ranking on i) surface preference, ii) surface defect formation energy, and iii) oxygen evolution.
- Favorable elements are found to be Nb, Ru, Ir, Sb, Os and Ta ; all preferentially occupying the surface rather than the bulk, having low surface defect formation energies and improved oxygen retention.

We will continue the study of the layered Li excess materials by

- Finalizing the investigation of surface doping elements and coordinating with PI Guoying Chen on the synthesis and testing of oxygen protection on Li-excess cathode surfaces.
- Screening and investigation of the amorphous coating materials.

Any proposed future work is subject to change based on funding levels.

Ongoing collaborative investigation with **Guoying Chen** (LBNL) on adding select dopants to cathode formulations and investigating its effect on oxygen retention and cathode performance.

Fruitful discussions with **Gerbrand Ceder** (UCB) on understanding degradation mechanisms in Li-excess materials are gratefully acknowledged.

Most Recent Reviewer Comments (2015)



Department of Energy
Office of Biological and Environmental Research

Presentation Title	Principal Investigator and Organization	Page Number	Approach	Technical Accomplishments	Collaborations	Future Research	Weighted Average
Predicting and Understanding Novel Electrode Materials From First Principles	Persson, Kristin (LBNL)	2-53	3.67	3.67	3.67	3.50	3.65

Representative (select) 2015 Review comments:

The project is shedding light on the stability and potential improvements that can be introduced into high capacity cathode powders. That, the reviewer continued, is very related to petroleum displacement, as it will enable higher capacity batteries.

...it will be interesting to know additional details of the redox process involving oxygen. The new edge path proposed for Mn⁴⁺ migration is a nice accomplishment that can be used for the design of high-capacity materials.

[Response: we thank the reviewers for the positive reviews. Most of the suggestions related to elucidating the process of oxygen release, which has indeed been a focus of 2016.](#)

The project team have produced extensive results on the cycling of the Li₂MnO₃ active material, the reviewer noted.

Excellent collaborations and synergies with other DOE laboratories and industry were noted by this reviewer.